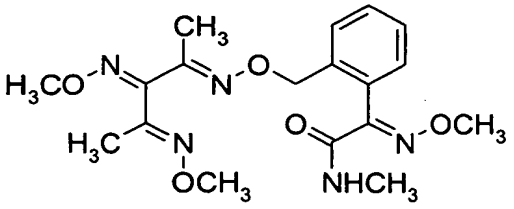
Fungicidal mixtures for controlling rice pathogens

The present invention relates to fungicidal mixtures for controlling rice pathogens, comprising, as active components

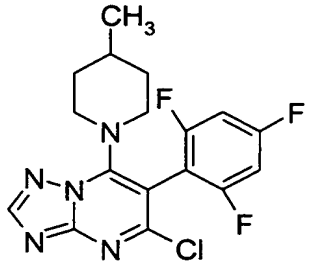
1) the compound of the formula I,



I

and

2) the compound of the formula II,



II

in a synergistically effective amount.

Moreover, the invention relates to a method for controlling rice pathogens using mixtures of the compound I with the compound II and to the use of the compound I with the compound II for preparing such mixtures and compositions comprising these mixtures.

The compound of the formula I, 2-[2-(2,3-bismethoxyimino-1-methylbutylideneamino-oxymethyl)phenyl]-2-methoxyimino-N-methylacetamide belongs to the class of the active strobilurin compounds, its preparation and its action against harmful fungi, in particular against rice diseases, is known (WO 97/15552; common name: orysastrobin).

The compound II, 5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, its preparation and its action against harmful fungi are likewise known from the literature (WO 98/46607).

Mixtures of orysastrobin with other active compounds are known (WO 99/48366, WO 99/48367).

Mixtures of triazolopyrimidines with various active compounds are known in a general manner from EP-A 988 790. Mixtures with synthetic strobilurin derivatives are embraced by the general disclosure.

The synergistic mixtures of triazolopyrimidine derivatives known from EP-A 988 790 are described as being fungicidally active against various diseases of cereals, fruit and vegetable, in particular mildew on wheat and barley or gray mold on apples.

Owing to the special cultivation conditions of rice plants, the requirements that a rice fungicide has to meet are considerably different from those that fungicides used in cereal or fruit growing have to meet. There are significant differences in the application method: in rice crops, the fungicide is usually applied directly onto the soil during or shortly after sowing. The fungicide is taken up into the plant via the roots and transported in the sap of the plant to the plant parts to be protected. For rice fungicides, high systemic action is therefore essential. In contrast, in cereal or fruit growing, the fungicide is usually applied onto the leaves or the fruits; accordingly, in these crops the systemic action of the active compounds is considerably less important.

Moreover, rice pathogens are typically different from those in cereals or fruit. *Pyricularia oryzae* and *Corticium sasakii* (syn. *Rhizoctonia solani* AG 1-IA) are the pathogens of the diseases most prevalent in rice plants. In other crop plants, they are not encountered to any degree worth mentioning. *Rhizoctonia solani* is the only pathogen of agricultural significance from the sub-class *Agaricomycetidae.* In contrast to most other fungi, this fungus attacks the plant not via spores but via a mycelium infection.

For these reasons, findings concerning the fungicidal activity of active compounds in the cultivation of cereals or fruit cannot be transferred to rice crops.

Orysastrobin is known as a specific rice fungicide.

It was an object of the present invention to provide, with a view to a more effective control of rice pathogens at application rates which are as low as possible, mixtures of orysastrobin which, at a reduced total amount of active compounds applied, have an improved effect against the harmful fungi.

We have found that this object is achieved by the combination of active compounds defined at the outset. Moreover, we have found that simultaneous, that is joint or separate, application of the compound I and the compound II or successive application of the compound I and the compound II allows better control of harmful fungi than is possible with the individual compounds.

When preparing the mixtures, it is preferred to employ the pure active compounds I and II, to which further active compounds against harmful fungi or other pests, such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active compounds or fertilizers can be added.

The mixtures of compounds I and II, or the compounds I and II used simultaneously, that is jointly or separately, exhibit outstanding action against harmful fungi from the classes of the *Ascomycetes*, *Deuteromycetes* and *Basidiomycetes*. They have high systemic action and can therefore be used for the treatment of seed and as foliar- and soil-acting fungicides.

They are especially important for controlling harmful fungi on rice plants and their seeds, such as *Bipolaris* and *Drechslera* species. They can be used particularly advantageously for controlling *Pyricularia oryzae*, the rice blast pathogen, and sheath blight on rice, caused by *Corticium sasakii* (syn. *Rhizoctonia solani*).

The compound I and the compound II can be applied simultaneously, that is jointly or separately, or in succession, the sequence, in the case of separate application, generally not having any effect on the result of the control measures.

The compound I and the compound II are usually applied in a weight ratio of from 100:1 to 1:100, preferably from 20:1 to 1:50, in particular from 5:1 to 1:20.

Depending on the desired effect, the application rates of the mixtures according to the invention are from 5 g/ha to 2000 g/ha, preferably from 50 to 1500 g/ha, in particular from 50 to 750 g/ha.

Correspondingly, the application rates of the compound I are generally from 1 to 1000 g/ha, preferably from 10 to 750 g/ha, in particular from 20 to 500 g/ha.

Correspondingly, the application rates of the compound II are generally from 1 to 1000 g/ha, preferably from 10 to 750 g/ha, in particular from 20 to 500 g/ha.

In the treatment of seed, the application rates of the mixture are generally from 0.001 to 1 g/kg of seed, preferably from 0.01 to 0.5 g/kg, in particular from 0.01 to 0.1 g/kg.

In the control of phytopathogenic harmful fungi, the separate or joint application of the compounds I and II or of the mixtures of the compounds I and II is carried out by spraying or dusting the seeds, the seedlings, the plants or the soils before or after sowing of the plants or before or after emergence of the plants. When used against rice pathogens, the compounds are applied jointly or separately, preferably by applying granules or by dusting the soils.

The mixtures according to the invention or the compounds I and II can be converted into the customary formulations, for example solutions, emulsions, suspensions, dusts, powders, pastes and granules. The application form depends on the particular purpose; in each case, it should ensure a fine and uniform distribution of the compound according to the invention.

The formulations are prepared in a known manner, for example by extending the active compound with solvents and/or carriers, if desired using emulsifiers and dispersants. Solvents/auxiliaries which are suitable are essentially:

- water, aromatic solvents (for example Solvesso products, xylene), paraffins (for example mineral fractions), alcohols (for example methanol, butanol, pentanol, benzyl alcohol), ketones (for example cyclohexanone, gamma-butyrolactone), pyrrolidones (NMP, NOP), acetates (glycol diacetate), glycols, fatty acid dimethylamides, fatty acids and fatty acid esters. In principle, solvent mixtures may also be used.
- carriers such as ground natural minerals (for example kaolins, clays, talc, chalk) and ground synthetic minerals (for example highly disperse silica, silicates); emulsifiers such as nonionic and anionic emulsifiers (for example polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignin-sulfite waste liquors and methylcellulose.

Suitable surfactants are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutylnaphthalenesulfonic acid, alkylarylsulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates, fatty acids and sulfated fatty alcohol glycol ethers, furthermore condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctylphenol, octylphenol, nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ether,

tristearylphenyl polyglycol ether, alkylaryl polyether alcohols, alcohol and fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lignin-sulfite waste liquors and methylcellulose.

Substances which are suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, cyclohexanol, cyclohexanone, isophorone, strongly polar solvents, for example dimethyl sulfoxide, N-methylpyrrolidone and water.

Powders, materials for spreading and dustable products can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.

Granules, for example coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active compounds to solid carriers. Examples of solid carriers are mineral earths such as silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, such as, for example, ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

In general, the formulations comprise from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active compounds. The active compounds are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

The following are examples of formulations: 1. Products for dilution with water

A) Soluble concentrates (SL)

10 parts by weight of the active compounds are dissolved in water or in a water-soluble solvent. As an alternative, wetters or other auxiliaries are added. The active compound dissolves upon dilution with water.

B) Dispersible concentrates (DC)

20 parts by weight of the active compounds are dissolved in cyclohexanone with addition of a dispersant, for example polyvinylpyrrolidone. Dilution with water gives a dispersion.

C) Emulsifiable concentrates (EC)

15 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength). Dilution with water gives an emulsion.

D) Emulsions (EW, EO)

40 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength). This mixture is introduced into water by means of an emulsifier (Ultraturax) and made into a homogeneous emulsion. Dilution with water gives an emulsion.

E) Suspensions (SC, OD)

In an agitated ball mill, 20 parts by weight of the active compounds are comminuted with addition of dispersant, wetters and water or an organic solvent to give a fine active compound suspension. Dilution with water gives a stable suspension of the active compound.

F) Water-dispersible granules and water-soluble granules (WG, SG)

50 parts by weight of the active compounds are ground finely with addition of dispersants and wetters and made into water-dispersible or water-soluble granules by means of technical appliances (for example extrusion, spray tower, fluidized bed). Dilution with water gives a stable dispersion or solution of the active compound.

G) Water-dispersible powders and water-soluble powders (WP, SP)

75 parts by weight of the active compounds are ground in a rotor–stator mill with addition of dispersant, wetters and silica gel. Dilution with water gives a stable dispersion or solution with the active compound.

2. Products to be applied undiluted

H) Dustable powders (DP)

5 parts by weight of the active compounds are ground finely and mixed intimately with 95% of finely divided kaolin. This gives a dustable product.

I) Granules (GR, FG, GG, MG)

0.5 part by weight of the active compounds is ground finely and associated with 95.5% carriers. Current methods are extrusion, spray-drying or the fluidized bed. This gives granules to be applied undiluted.

J) ULV solutions (UL)
10 parts by weight of the active compounds are dissolved in an organic solvent, for example xylene. This gives a product to be applied undiluted.

The active compounds can be used as such, in the form of their formulations or the use forms prepared therefrom, for example in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dustable products, materials for spreading, or granules, by means of spraying, atomizing, dusting, spreading or pouring. The use forms depend entirely on the intended purposes; it is intended to ensure in each case the finest possible distribution of the active compounds according to the invention.

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of a wetter, tackifier, dispersant or emulsifier. Alternatively, it is possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

The active compound concentrations in the ready-to-use preparations can be varied within relatively wide ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

The active compounds may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active compound, or even to apply the active compound without additives.

Various types of oils, wetters, adjuvants, herbicides, fungicides, other pesticides, or bactericides may be added to the active compounds, if appropriate just immediately prior to use (tank mix). These agents can be admixed with the agents according to the invention in a weight ratio of 1:10 to 10:1.

The compounds I and II or the mixtures or the corresponding formulations are applied by treating the harmful fungi or the plants, seeds, soils, areas, materials or spaces to be kept free from them with a fungicidally effective amount of the mixture or, in the case of separate application, of the compounds I and II. Application can be carried out before or after infection by the harmful fungi.

The fungicidal action of the compound and the mixtures can be demonstrated by the experiments below:

The active compounds, separately or jointly, were prepared as a stock solution with 0.25% by weight of active compound in acetone or DMSO. 1% by weight of the emulsifier Uniperol® EL (wetting agent having emulsifying and dispersing action based on ethoxylated alkylphenols) was added to this solution, and the solution was diluted with water to the desired concentration.

Use example – protective activity against rice blast caused by *Pyricularia oryzae*

Leaves of rice seedlings of the cultivar "Tai-Nong 67", which had been grown in pots, were sprayed to runoff point with an aqueous suspension having the concentration of active compounds stated below. The next day, the plants were inoculated with an aqueous spore suspension of *Pyricularia oryzae*. The test plants were then placed in climatized chambers at 22-24°C and 95-99% relative atmospheric humidity for 6 days. The extent of the development of the infection on the leaves was then determined visually.

Evaluation was carried out by determining the infected leaf areas in percent. These percentages were converted into efficacies.

The efficacy (E) is calculated as follows using Abbot's formula:

$$E = (1 - \alpha/\beta) \cdot 100$$

α corresponds to the fungicidal infection of the treated plants in % and

β corresponds to the fungicidal infection of the untreated (control) plants in %

An efficacy of 0 means that the infection level of the treated plants corresponds to that of the untreated control plants; an efficacy of 100 means that the treated plants were not infected.

The expected efficacies of the mixtures of active compounds are determined using Colby's formula [R.S. Colby, Weeds 15, 20-22 (1967)] and compared with the observed efficacies.

Colby's formula:

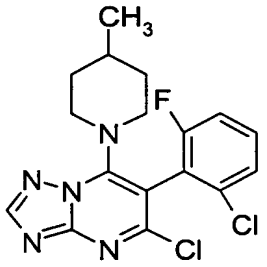
$$E = x + y - x \cdot y/100$$

E expected efficacy, expressed in % of the untreated control, when using the mixture of the active compounds A and B at the concentrations a and b

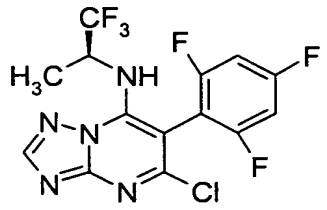
x efficacy, expressed in % of the untreated control, when using active compound A at the concentration a

y efficacy, expressed in % of the untreated control, when using active compound B at the concentration b

The comparative compounds used were compounds A and B, suggested in EP-A 988 790 for mixtures with synthetic strobilurin derivatives:



A



B

Table A – Individual active compounds

Example	Active compound	Concentration of active compound in the spray liquor [ppm]	Efficacy in % of the untreated control
1	Control (untreated)	-	(83% infection)
2	I (orysastrobin)	4 0.25	28 0
3	II	4 1	52 3
4	Comparative compound A	4 1	28 0
5	Comparative compound B	4 1	52 28

Table B – Mixtures according to the invention

Example	Mixture of active compounds; concentration; mixing ratio	Observed efficacy	Calculated efficacy*)
6	I + II 0.25 + 4 ppm 1:16	82	52
7	I + II 1 + 0.25 ppm 4:1	76	30

*) efficacy calculated using Colby's formula

Table C – Comparative experiments – mixtures with compounds A and B suggested in EP-A 988 790 for mixtures with strobilurin derivatives

Example	Mixture of active compounds concentration mixing ratio	Observed efficacy	Calculated efficacy*)
8	I + A 0.25 + 4 ppm 1 : 16	0	28
9	I + A 1 + 0.25 ppm 4:1	0	28
10	I + B 0.25 + 4 ppm 1 : 16	40	52
11	I + B 1 + 0.25 ppm 4:1	28	48

*) efficacy calculated using Colby's formula

The test results show that the mixtures according to the invention of orysastrobin and the triazolopyrimidine derivative II show considerably increased activity, whereas, at comparable application rates, the mixtures with compounds A and B, suggested in EP-A 988 790, have at most weak activity.